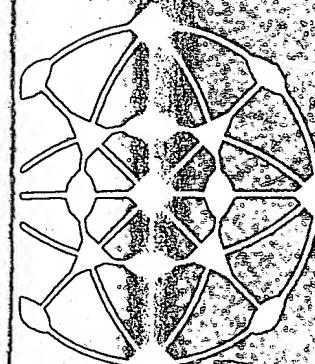


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## Oxygen Defect $K_2NiF_4$ -Type Oxides: The Compounds $La_{2-x}Sr_xCuO_{4-x/2+\delta}$

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Oxygen defect  $K_2NiF_4$ -type oxides  $La_{2-x}Sr_xCuO_{4-x/2+\delta}$  have been synthesized for a wide composition range:  $0 \leq x \leq 1.34$ . From the X-ray and electron diffraction study three domains have been characterized: orthorhombic compounds with  $La_2CuO_4$  structure for  $0 \leq x < 0.10$ , tetragonal oxides similar to  $LaSrCuO_4$  for  $0.10 \leq x < 1$  and several superstructures derived from the tetragonal cell ( $a = n \cdot a_{LaSrCuO_4}$  with  $n = 3, 4, 4.5, 5, 6$ ) for  $1 \leq x \leq 1.34$ . The compounds corresponding to  $0 < x < 1$  differ from the other oxides in that they are characterized by the presence of copper with two oxidation states: +2 and +3. A model structure for  $La_{0.8}Sr_{1.2}Cu\lambda O_{3.4}$ , in which copper has only the +2 oxidation state, and for which the actual cell is tetragonal— $a = 18.80 \text{ \AA}$  and  $c = 12.94 \text{ \AA}$ —has been established. The particular structural evolution of these compounds is discussed in terms of a competition between the capability of Cu(II) to be oxidized to Cu(III) and the ordering of oxygen vacancies.

### Introduction

A lot of oxides, with the  $A_2MO_4$  formula, characterized by the intergrowth of perovskite- and sodium chloride-type layers are known at the present time. Contrary to the perovskite oxides, no oxygen defect has been observed for this structural series to our knowledge. Copper, due to its ability to take different coordinations smaller than six, is a potential candidate which could form such anion defect compounds. However the only isostructural copper compounds which have been synthesized,  $La_2CuO_4$  (1, 2) and  $SrLaCuO_4$  (3) are stoichiometric. Nevertheless, the recent results concerning the oxides  $La_{2-x}A_{1+x}O_{6-x/2}$  ( $A = Ca, Sr$ ) (4), whose

structure is strongly related to that of  $Sr_3Ti_2O_7$  (5) suggest the possibility of oxygen defect for  $A_2CuO_4$  compounds. Thus, the present work deals with the oxides  $La_{2-x}Sr_xCuO_{4-x/2+\delta}$ , for which the replacement of lanthanum by strontium leads to the formation of oxygen vacancies, involving order phenomena.

### Experimental

For the synthesis of the compounds of the system  $La_2CuO_4-Sr_2CuO_3$ ,  $SrCO_3$ ,  $CuO$  and  $La_2O_3$  were mixed according to the following ratios:  $(2 - x)/2La_2O_3/x SrCO_3/1 CuO$ . All these reactions were made in a platinum crucible in air. The synthesis of the compounds with high purity strongly depends on the temperature for a fixed pressure. The mixtures were thus first heated for 5 hr at  $900^\circ C$ , and then at tem-

peratures ranging 12 hr.

The oxidation s oxygen defect, was the compounds by réactions were followed using a Setaran

The crystallography was established by two com ray diffractometry with a Philips goniometer and fraction using an scope.

### Results

#### Study of the System The Compounds $La_{2-x}Sr_xCuO_{4-x/2+\delta}$

According to the scribed,  $K_2NiF_4$ -tj sponding to the  $La_{2-x}Sr_xCu^{II}O_{4-x/2}$  large composition r. microthermogravim ides under hydrog that a part of Cu(I)

Range	$x$
I	0
	0.08
II	0.25
	0.33 <sup>a</sup>
	0.50
	0.66 <sup>a</sup>
III	0.88 <sup>a</sup>
	1.00 <sup>a</sup>
	1.28 <sup>a</sup>
	1.34 <sup>a</sup>
	1.20
	0.0

<sup>a</sup> The "a" parameters composition are given in

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peratures ranging from 1000 to 1200°C for 12 hr.

The oxidation state of copper, i.e., the oxygen defect, was determined by reducing the compounds by hydrogen: the reduction reactions were followed by thermogravimetry using a Setaram microbalance.

The crystallographic data were established by two complementary methods: X-ray diffractometry using  $CuK\alpha$  radiation with a Philips goniometer and electron diffraction using an EM 200 Philips microscope.

## Results

### *Study of the System $La_2CuO_4-Sr_2CuO_3$ : The Compounds $La_{2-x}Sr_xCuO_{4-x/2+\delta}$*

According to the methods previously described,  $K_2NiF_4$ -type compounds corresponding to the nominal composition  $La_{2-x}Sr_xCu^{II}O_{4-x/2}$  were synthesized in a large composition range:  $0 \leq x \leq 1.34$ . The microthermogravimetric study of these oxides under hydrogen showed, however, that a part of Cu(II) had been oxidized to

Cu(III), leading to the formula  $La_{2-x}Sr_xCuO_{4-x/2+\delta}$  with  $0 \leq \delta < 0.12$ . For  $x > 1.34$  a mixture of the  $K_2NiF_4$ -type phase and  $Sr_2CuO_3$  (6) was observed.

The crystallographic data of different compositions are summarized in Table I. The study of the X-ray patterns showed a continuous evolution of the structure and allowed to characterize three composition ranges which were studied by electron diffraction.

(I)  $0 \leq x < 0.10$ . The X-ray patterns very similar to that of  $La_2CuO_4$  (1) were indexed in an orthorhombic cell with:

$$a_1 = 2a_p \sin \beta/2 = a_{La_2CuO_4},$$

$$b_1 = 2a_p \cos \beta/2 = b_{La_2CuO_4},$$

$$c_1 \approx c_{La_2CuO_4},$$

where  $a_p$  is the parameter of the perovskite cubic cell, and  $\beta$  defines the monoclinic distortion of the cell.

From the conditions limiting possible reflections— $hkl : h+k, l+h, k+l = 2n$ —three space groups are possible:  $Fmmm$ ,  $Fmm2$ , and  $F222$ .

TABLE I  
CRYSTALLOGRAPHIC DATA OF  $La_{2-x}Sr_xCuO_{4-x/2+\delta}$  COMPOUNDS

Range	$x$	$\delta$	Composition	$a$ (Å)	$b$ (Å)	$c$ (Å)	Heating temperature (°C)
I	0	0	$La_2CuO_4$	5.366(2)	5.402(2)	13.149(4)	1100
	0.08	0.030(1)	$La_{1.92}Sr_{0.08}CuO_{3.99}$	5.351(1)	5.368(2)	13.200(5)	1000
II	0.25	0.060(4)	$La_{1.75}Sr_{0.25}CuO_{3.93}$	3.775(2)		13.247(5)	1000
	0.33 <sub>3</sub>	0.119(4)	$La_{1.66}Sr_{0.33}CuO_{3.95}$	3.776(1)		13.250(2)	1100
	0.50	0.100(4)	$La_{1.50}Sr_{0.50}CuO_{3.85}$	3.773(1)		13.204(3)	1160
	0.66 <sub>6</sub>	0.092(4)	$La_{1.33}Sr_{0.66}CuO_{3.75}$	3.775(1)		13.150(4)	1170
	0.88 <sub>0</sub>	0.088(4)	$La_{1.12}Sr_{0.88}CuO_{3.64}$	3.773(1)		13.073(5)	1170
III	1.00 <sup>a</sup>	0.0	$LaSrCuO_{3.50}$	3.767(1)		13.002(3)	1200
	1.28 <sup>a</sup>	0.0	$La_{0.72}Sr_{1.28}CuO_{3.36}$	3.761(2)		12.922(9)	1200
	1.34 <sup>a</sup>	0.0	$La_{0.66}Sr_{1.34}CuO_{3.33}$	3.759(3)		12.907(9)	1200
	1.20	0.0	$La_{0.80}Sr_{1.20}CuO_{3.40}$	18.803(7)		12.941(7)	1200

<sup>a</sup> The "a" parameters of these compounds (range III) are those of the tetragonal subcell;  $n$  values for every composition are given in Table II.

(II)  $0.10 \leq x < 1$ . The symmetry is tetragonal like that of  $\text{LaSrCuO}_4$  (3); the cell parameters are related to the latter and to I in the following manner:

$$a_{\text{II}} = a_{\text{I}}/2^{1/2} \approx a_{\text{P}} = a_{\text{LaSrCuO}_4},$$

$$c_{\text{II}} \sim c_{\text{I}} \sim c_{\text{LaSrCuO}_4}.$$

The reflection conditions are those of  $\text{LaSrCuO}_4 - hkl : h + k + l = 2n$ —involving the space groups:  $I4/mmm$ ,  $I4/m$ ,  $I422$  and  $I42m$ .

(III)  $1 \leq x \leq 1.34$ . The X-ray diffractograms are characterized by the existence of a system of strong peaks, which was already observed for the compounds (II), involving at least the existence of a tetragonal subcell of the same type. However, for all these patterns, weak peaks were always observed which could not be indexed in this cell. An electron diffraction study was thus undertaken: about 50 crystals were examined for each value of  $x$  given in Table II. Several types of crystals were isolated:

—Small number of crystals, about 10%, were characterized by a tetragonal cell similar to that of  $\text{LaSrCuO}_4$ :

$$a_{\text{III}} \sim a_{\text{II}} \sim a_{\text{P}} \sim a_{\text{LaSrCuO}_4},$$

$$c_{\text{III}} \approx c_{\text{II}} \approx c_{\text{I}} \sim c_{\text{LaSrCuO}_4}.$$

—Most of the crystals, i.e., about 90%, presented, in addition to the fundamental reflections previously described, superstructure reflections with a variable inten-

sity. The electron diffraction patterns allowed us to find the following relations for the actual tetragonal cell for a composition  $x$ :

$$a_{\text{III}}^x = na_{\text{III}} \sim na_{\text{II}},$$

$$c_{\text{III}}^x = c_{\text{III}} \# c_{\text{II}} \approx c_{\text{I}}.$$

For a same composition  $x$ , several sorts of superstructures were generally observed, characterized either by integral  $n$  values ( $n = 4, 5$ , or 6) or nonintegral values of  $n$  ( $n$  ranging from 4.5 to 5.6), as shown for several compositions in Table II. Figure 1 shows, as an example, the electron diffraction patterns of the (001) planes for  $\text{La}_{2/3}\text{Sr}_{4/3}\text{CuO}_{3.33}$ . From Table II it can be seen that a pure term, characterized by a superstructure with an integral value of  $n$  ( $n = 5$ ), is only obtained for  $x = 1.20$ . It has thus been attempted to elaborate a structural model for this phase.

#### A Structural Model for $\text{La}_{0.8}\text{Sr}_{1.2}\text{CuO}_{3.4}$

The actual cell of this compound is tetragonal:  $a = 18.80_4 \text{ \AA}$  and  $c = 12.94 \text{ \AA}$  ( $Z = 50$ ). The conditions limiting possible reflections are the same as those of the subcell ( $a = 3.760$ ,  $c = 12.94 \text{ \AA}$ ;  $Z = 2$ ), leading to the space groups  $I4/mmm$ ,  $I4/m$ ,  $I422$ , and  $I42m$ . The intensity calculations were first made in the  $\text{K}_2\text{NiF}_4$  type cell, with the most symmetric space group  $I4/mmm$ . For these calculations, reflections corresponding only to the subcell were used. Copper atoms were placed on 2(a), lanthanum and strontium atoms were statistically distributed on 4e, and oxygen atoms and anionic vacancies were statistically distributed over two sorts of sites 4e ( $\text{O}_1$ ) and 4c ( $\text{O}_2$ ). After refinement of the atomic parameters the discrepancy factor could not be lowered below  $R = 0.104$ . The possibility of an order of the oxygen atoms and vacancies over the  $\text{O}_1$  and  $\text{O}_2$  sites was thus considered. The occupancy factors of both sites

FIG. 1. Electron dif  
(d) 6.

were refined successively and the best (Table IV) was obtained.

TAB  
 $\text{La}_{0.80}\text{Sr}_{1.20}\text{O}_{3.40}$ : ATOM PCT

	Sites	$x$	$y$
La	4(e)	0	0
Sr	2(a)	0	0
Cu	4(e)	0	0
O <sub>1</sub>	4(c)	0	0.5
O <sub>2</sub>			

<sup>a</sup>  $a = 3.760 \text{ \AA}$ ;  $c = 12.94 \text{ \AA}$ .

TABLE II  
 $n$  VALUES OBSERVED BY ELECTRON DIFFRACTION FOR COMPOUNDS OF RANGE III

Composition	$x$	$n$
$\text{LaSrCuO}_{3.5}$	1.00	1; 4.5
$\text{La}_{0.88}\text{Sr}_{1.12}\text{CuO}_{3.44}$	1.12	1; 4.5; 5
$\text{La}_{0.80}\text{Sr}_{1.20}\text{CuO}_{3.40}$	1.20	5
$\text{La}_{0.72}\text{Sr}_{1.28}\text{CuO}_{3.36}$	1.28	1; 4.6; 5; 5.3; 5.4
$\text{La}_{0.66}\text{Sr}_{1.34}\text{CuO}_{3.33}$	1.34	1; 4; 5; 5.6; 6

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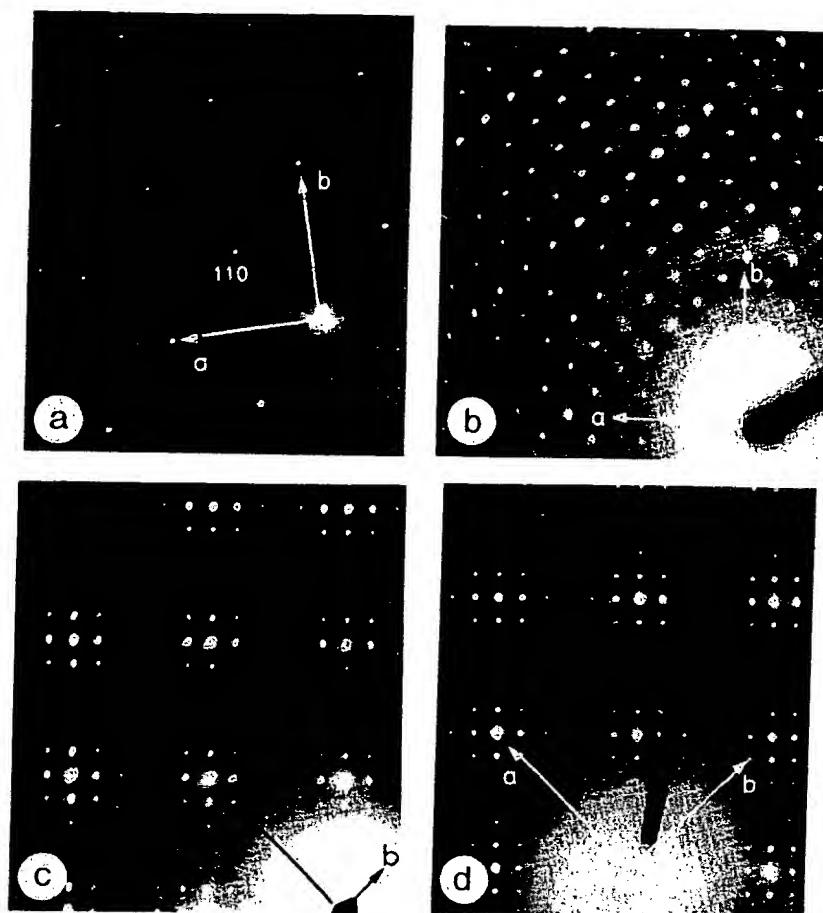


FIG. 1. Electron diffraction patterns of the (001) planes for  $\text{La}_{2/3}\text{Sr}_{4/3}\text{CuO}_{3.33}$ : (a)  $n = 1$ ; (b) 4; (c) 5.6; (d) 6.

were refined successively and then simultaneously and the best value of  $R = 0.081$  (Table IV) was obtained for a total occupa-

tion of the  $O_I$  sites, while vacancies and oxygen atoms were distributed over the  $O_{II}$  sites. The location of the vacancies preferentially on the  $O_{II}$  sites, at the same level as the copper atoms, can be considered as significant, on account of the relatively weak scattering factor of oxygen. This is confirmed by the high  $R$  value ( $R = 0.153$ ) obtained for a total occupation of the  $O_{II}$  sites, vacancies and oxygen atoms being distributed on the  $O_I$  sites. The first results which are summarized in Table III show the atoms are located in positions very close to those usually observed in  $K_2NiF_4$  type structures. The main difference with

TABLE III  
 $\text{La}_{0.80}\text{Sr}_{1.20}\text{O}_{3.40}$ : ATOM POSITIONS IN THE SUBCELL<sup>a</sup>

Sites	$x$	$y$	$z$	$B$ ( $\text{\AA}^2$ )
La	4(e)	0	0	$0.357 \pm 0.001$
Sr	4(e)	0	0	0.88
Cu	2(a)	0	0	0.85
$O_I$	4(e)	0	$0.168 \pm 0.002$	1.68
$O_{II}$	4(c)	0	0.5	4.25

<sup>a</sup>  $a = 3.760 \text{ \AA}$ ;  $c = 12.94 \text{ \AA}$ .

TABLE IV  
 $\text{La}_{0.8}\text{Sr}_{1.2}\text{CuO}_{3.4}$ : OBSERVED AND  
 CALCULATED INTENSITIES FOR ATOMIC  
 POSITIONS OF TABLE III<sup>a</sup>

$h \ k \ l$	$I_{\text{obs}}$	$I_{\text{calc}}$
0 0 2	4.0	4.0
1 0 1	13.0	15.1
0 0 4	17.0	16.9
1 0 3	164.0	156.1
1 1 0	114.0	115.1
1 1 2	0.1	1.7
0 0 6	29.0	23.6
1 0 5	27.0	23.5
1 1 4	35.0	34.6
2 0 0	44.0	49.8
2 0 2	0.1	0.4
1 1 6	26.0	25.2
2 1 1	3.9	3.8
1 0 7	12.0	11.1
2 0 4	10.3	8.2
0 0 8	6.6	5.3
2 1 3	48.0	48.1
2 0 6	15.8	18.1
2 1 5	8.1	9.4
1 1 8	9.0	7.5
1 0 9	0.1	1.7
2 2 0	9.0	12.4
2 2 2	0.1	0.1
0 0 10	0.1	0.8
3 0 1	0.1	0.7
2 1 7	6.0	7.0
2 2 4	3.3	3.0
2 0 8	7.6	6.9
3 0 3	7.0	8.8

<sup>a</sup> Subcell, space group  $I4/mmm$ ;  $R = 0.081$ .

the ideal structure concerns the existence of vacancies located in the same plane as the copper atoms (Fig. 2). Moreover, the high  $B$  value for oxygen of  $O_1$  sites ( $4.2 \text{ \AA}^2$ ) suggests that in this plane oxygen and vacancies were ordered.

Calculations in the actual cell in space group  $I4/m$ , were undertaken with 136 possible reflections, including superstructure reflections. Using the position and distributions determined from the subcell, the  $R$  factor increased to 0.104, showing, of course, a weak contribution of the superstructure reflections to the  $R$  value. The

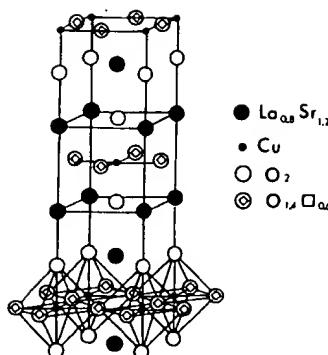


FIG. 2. Ideal drawing of the tetragonal  $K_2NiF_4$ -type structure showing the localization of oxygen vacancies for  $\text{La}_{0.8}\text{Sr}_{1.2}\text{CuO}_{3.4}$ .

atomic parameters were then refined and the  $R$  value was lowered to 0.07 for the final atomic parameters given in Table V. From this table it can be seen that copper atoms are not significantly displaced from their ideal positions, while the bigger cations La, Sr, and the oxygen atoms are only slightly displaced from their ideal positions, but enough to produce the superstructure reflections. These small displacements are certainly induced by an order of the oxygen vacancies, whose contribution to intensities is too small to be detected here. Thus, on account of the numerous possibilities of order between vacancies, and oxygen atoms, and of the weak scattering power of these atoms, we did not try any hypothesis of distribution. Nevertheless, the very likely ordering of vacancies in the "copper plane," should also involve an ordering of lanthanum and strontium over the different sites. Refining the occupancy factors of La and Sr, led to an  $R$  value of 0.064 which is not very significant due to the weak contribution of La and Sr to the superstructure reflexions; a preferential occupation of the different sites is, however, likely:  $A_1$ ,  $A_4$ , and  $A_5$  would only be occupied by strontium, while lanthanum would occupy 90% of  $A_6$  sites, the remaining strontium and lanthanum atoms being located statistically over the  $A_2$  and  $A_3$  sites.

T. $\text{La}_{0.8}\text{Sr}_{1.2}\text{SuO}_{3.4}$ : AT ACT	Sites	x
$A_1(4e)$	0	
$A_2(16n)$	0.194	
$A_3(16n)$	0.403	
$A_4(16m)$	0.200	
$A_5(16m)$	0.410	
$A_6(32O)$	0.389	
$A_7(2a)$	0	
$A_8(8i)$	0.200	
$A_9(8i)$	0.400	
$A_{10}(8h)$	0.200	
$A_{11}(8h)$	0.405	
$A_{12}(16l)$	0.403	
$A_{13}(4e)$	0	
$A_{14}(16n)$	0.216	
$A_{15}(16n)$	0.382	
$A_{16}(16m)$	0.182	
$A_{17}(16m)$	0.400	
$A_{18}(32O)$	0.400	
$A_{19}(8i)$	0.100	
$A_{20}(8i)$	0.300	
$A_{21}(4c)$	0	
$A_{22}(16l)$	0.214	
$A_{23}(16l)$	0.430	
$A_{24}(16l)$	0.300	
$A_{25}(16l)$	0.390	
$A_{26}(8j)$	0.200	
$A_{27}(8j)$	0.400	

<sup>a</sup>  $a = 18.804 \text{ \AA}$ ;  $c = I_4/mmm$ .

## Discussion

The stabilization,  $\text{Cu(III)}$  by only heating is worthy of note. But the characteristic of this existence of a  $\text{Cu(III)}$   $< x < 1$  which lies in regions ( $x = 0$  and  $1$ ) strongly related one to another can be explained by two reasons: (1)  $\text{Cu(III)}$  and  $\text{Cu(II)}$  are competitive: the stoichiometric  $\text{K}_2\text{NiF}_4$ ,  $\text{La}_2\text{CuO}_4$  and  $\text{LaSrCuO}_3$  form a related defect

TABLE V  
 $La_{0.8}Sr_{1.2}CuO_{3.4}$ : ATOMIC PARAMETERS OF THE  
 ACTUAL CELL<sup>a</sup>

Sites	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ( $\text{\AA}^2$ )
$A_1(4e)$	0	0	0.347	0.35
$A_2(16n)$	0.194	0	0.359	1.00
$A_3(16n)$	0.403	0	0.356	0.39
$A_4(16m)$	0.200	0.200	0.357	0.32
$A_5(16m)$	0.410	0.410	0.358	1.00
$A_6(32O)$	0.389	0.192	0.357	0.86
$A_7(2a)$	0	0	0	0.80
$A_8(8i)$	0.200	0	0	0.51
$A_9(8i)$	0.400	0	0	0.43
$A_{10}(8h)$	0.200	0.200	0	0.31
$A_{11}(8h)$	0.405	0.405	0	1.00
$A_{12}(16f)$	0.403	0.205	0	0.37
$A_{13}(4e)$	0	0	0.168	1.00
$A_{14}(16n)$	0.216	0	0.168	1.00
$A_{15}(16n)$	0.382	0	0.168	1.00
$A_{16}(16m)$	0.182	0.182	0.172	1.00
$A_{17}(16m)$	0.400	0.400	0.168	1.00
$A_{18}(32O)$	0.400	0.202	0.163	1.00
$A_{19}(8i)$	0.100	0	0	1.00
$A_{20}(8i)$	0.300	0	0	1.00
$A_{21}(4c)$	0	0.500	0	1.00
$A_{22}(16f)$	0.214	0.100	0	1.00
$A_{23}(16f)$	0.430	0.100	0	1.00
$A_{24}(16f)$	0.300	0.200	0	1.00
$A_{25}(16f)$	0.390	0.310	0	1.00
$A_{26}(8j)$	0.200	0.500	0	1.00
$A_{27}(8j)$	0.400	0.500	0	1.00

<sup>a</sup>  $a = 18.804 \text{ \AA}$ ;  $c = 12.941 \text{ \AA}$  (space group  $I_4/mmm$ ).

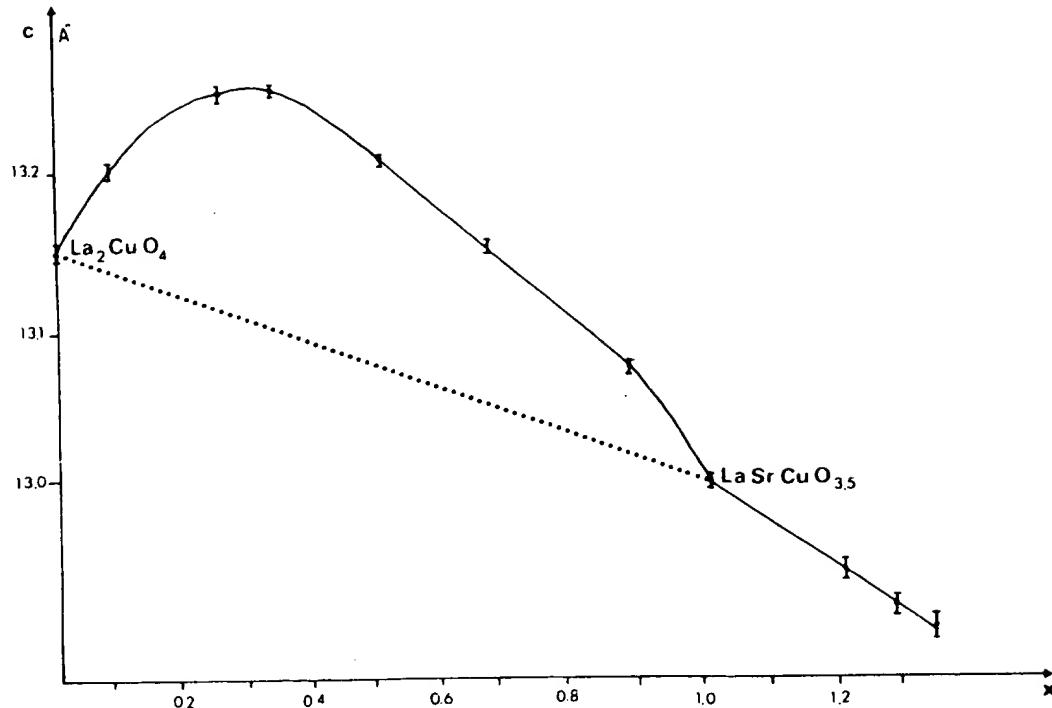
### Discussion

The stabilization, in this system, of Cu(III) by only heating the oxides in air is worthy of note. But the most important characteristic of this system concerns the existence of a Cu(III) composition range ( $0 < x < 1$ ) which lies between two Cu(II) regions ( $x = 0$  and  $x \geq 1$ ), for structures strongly related one to the other. This can be explained by two opposite effects which are competitive: the trend to preserve a stoichiometric  $K_2NiF_4$  structure as for  $La_2CuO_4$  and  $LaSrCuO_4$  and the trend to form a related defect structure but with an

ordering of the oxygen vacancies. Thus, rather close to the stoichiometric compound  $La_2CuO_4$  ( $x < 1$ ), the trend to stoichiometry is favored and the vacancies formed from the nominal compositions involving only Cu(II) are partly balanced by the oxidation of Cu(II) to Cu III. For  $x \geq 1$ , i.e., rather far from stoichiometry, the  $La_2CuO_4$  or "LaSrCuO<sub>4</sub>" stoichiometric compounds cannot be stabilized any more and orderings of the oxygen vacancies appear leading to different microphases as observed from the electron diffraction study, favoring Cu(II) with smaller coordinations (2, 5).

Structure is not, of course, the only factor governing the relative stability of Cu(II) and Cu(III) in these oxides. Kinetics play an important part for determining the ratio Cu(III)/Cu(II) in the richer Cu(III) oxides. For  $0 < x < 1$ , we have indeed noticed that the pure compounds could only be synthesized by heating at least 12 hr at the formation temperature (Table I) in order to ensure a good crystallization. Annealing the same samples at the same temperature, during longer periods (24 hr) allows us to prepare pure phases with the same structure, but with greater amount of Cu(III). The oxygen pressure will also influence the Cu(III)/Cu(II) ratios. Heating, for example, some Cu(III) samples at low temperature under vacuum, involves a decrease of Cu(III) amount without destroying the structure. In the same way, a reaction under oxygen allows us to increase the Cu(III) amount.

The influence of the Cu(III) amount can also be detected by considering the structural evolution, especially the *c* parameter, of these compounds as a function of composition (Fig. 3). This evolution is rather complex and quite different from that usually observed for single solid solutions. The substitution of strontium for lanthanum, should not affect this evolution, due to the similar sizes of these cations. It seems interesting to take the Cu(II) compounds as

FIG. 3. Evolution of the "c" parameter as a function of  $x$ .

a reference (dotted lines). Although we have only our compositions for comparison it can be seen that from  $\text{La}_2\text{Cu}^{\text{II}}\text{O}_4$  to  $\text{La}_{0.7}\text{Sr}_{1.3}\text{Cu}^{\text{II}}\text{O}_{3.35}$ , a continuous decrease of  $a$  and  $c$  parameters could be foreseen for all Cu(II) compounds, as  $x$  increases, in agreement with the increase of oxygen vacancies. This evolution is not linear, probably due to ordering of the vacancies observed for different compositions. What is worthy of note is the large deviation from this law observed for the only compounds containing Cu(III) (continuous line): the  $c$  parameter is greater than that obtained from the "reference line" corresponding to the presence of Cu(II) only, while the  $a$  parameter is smaller. Moreover, the largest deviations are observed for  $x = 0.33$  which corresponds to the maximum value of  $\delta$  ( $\delta = 0.119$ ), i.e., for the greatest amount of Cu(III). It can thus be observed that the  $c/a$

ratio increases with the Cu(III)/Cu(II) ratio in agreement with the observations previously made by Goodenough *et al.* (3). Attempts to modify the  $a$  and  $c$  parameters for  $x = 0.16$  and  $0.5$ , were successful: heating these compounds under vacuum at  $500^\circ\text{C}$  led to a decrease of  $c$  and a slight increase of  $a$ , while a decrease of the Cu(III)/Cu(II) ratio was confirmed.

### Conclusion

The stabilization of a great number of oxygen vacancies in the  $\text{K}_2\text{NiF}_4$ -type structure has been shown. It is easily explained by the ability of copper to show square and square-pyramidal coordinations. During the synthesis in air, two phenomena are competitive: the substitution of  $\text{Cu}^{3+}$  for  $\text{Cu}^{2+}$ , and ordering of oxygen and vacancies involving the existence of microphases.

The influence of the oxygen vacancies on the formation of these structures will be investigated. The relations between the properties and the structure will be studied.

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The influence of the oxygen pressure on the formation of these structures will be investigated. The relations between the electrical properties and the structure of these oxides will be studied.

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